

Analysis of Impurities in Semiconductor Grade Sulfuric Acid Using the Agilent 7500cs ICP-MS

Application

Semiconductor

Author

Junichi Takahashi
Kouichi Youno
Agilent Technologies
9-1 Takakura-Cho, Hachioji-Shi
Tokyo, 192-0033
Japan

Abstract

This application note demonstrates the suitability of a newly developed, high sensitivity reaction cell inductively coupled plasma mass spectrometer (ICP-MS) for the determination of inorganic impurities in semiconductor grade sulfuric acid. The Agilent 7500cs ICP-MS, featuring a high sensitivity version of the Octopole Reaction System (ORS), was used to analyze sulfuric acid for all the metals required by the semiconductor industry. The enhanced ORS eliminates all plasma and matrix based polyatomics that interfere with the measurement of elements such as K, Ca, Ti, Cr, Fe, Co, Ni, Cu, and Zn while offering excellent ion transmission and sensitivity. Furthermore, all analytes can be measured at high plasma power to promote complete decomposition of the sulfuric acid in the plasma. This leads to high signal stability and a reduced frequency of routine maintenance. Sample preparation is a simple 10x dilution followed by direct analysis thereby significantly reducing the potential for the sample contamination frequently encountered with evaporative matrix elimination techniques.

Introduction

The determination of inorganic impurities in the high purity reagents used in the manufacture of semiconductor devices has become more important than ever before. The continued development of ultra-large-scale-integration semiconductor devices (ULSI) has resulted in an increase in component density, which in turn increases the frequency of failures due to the mobility of trace metal impurities in the device. Since the reagents used in the production process are a significant source of contamination, reagent vendors are continually working to develop products with lower levels of inorganic impurities. Sulfuric acid (H_2SO_4) is commonly used for cleaning of wafer surfaces. Combined with hydrogen peroxide, it effectively removes any organic residues.

Interference Removal

Matrix-based polyatomic overlaps present specific analytical problems for conventional quadrupole ICP-MS where ultratrace analysis is required in complex sample matrices. With the introduction of the high-sensitivity 7500cs collision/reaction cell ICP-MS, analysts can attenuate matrix interferences using a controlled collision/reaction environment within the ORS cell, which is pressurized with simple cell gases hydrogen (reaction mode) and helium (collision mode).



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Analysis of H₂SO₄

H₂SO₄ is now available with very low levels of impurities (<1 µg/L). The determination of impurities at these levels in H₂SO₄ is particularly challenging for two reasons. First, the high viscosity and high boiling point of H₂SO₄ make direct analysis difficult, so the sample matrix is often removed by evaporation prior to analysis. This approach requires a potentially time consuming sample preparation step as well as introducing the possibility of sample contamination. Second, while cool plasma ICP-MS has been used successfully to remove plasma based interferences Ar, ArH, ArO, on Ca, K, and Fe respectively, S-based matrix interferences (shown in Table 1) interfere with important elements such as Ti, Cr, Co, Ni, Cu, and Zn when direct analysis is performed.

Table 1. Sulfur-based Polyatomic Interferences on Ti, Cr, Ni, Cu, and Zn

Polyatomic ions	Mass	Analyte
SN	46	Ti
SNH	47	Ti
SO, SN	48	Ti
SOH	49	Ti
SOH ₂ , SO	50	Ti, Cr
SO	52	Cr
SCO	60	Ni
SNOH	63	Cu
SO ₂ , S ₂	64	Zn
SO ₂ H, S ₂ H	65	Cu
SO ₂	66	Zn
SO ₂	68	Zn

The 7500cs is able to remove these S-based interferences, greatly reducing the Background Equivalent Concentration (BEC) for the semiconductor critical elements titanium, copper, and zinc - even in 10% w/w H₂SO₄. A performance comparison with the non-cell 7500s, is presented in Table 2: BEC reduction with the ORS is two-three orders of magnitude. Note that all measurements are made directly on the analyte mass. Another approach to measuring Ti and Zn in H₂SO₄ is to use NH₃ as the reaction gas to complex with the analytes, and measure the resulting clusters at mass 114 and 115 respectively, but this strategy is not ideal since Cd, Sn, and In respectively, have isotopes at these masses.

Table 2. Comparison of ORS-Based Performance (7500cs) with Non-reaction Cell Performance (7500s)

Matrix: 9.8% w/w H₂SO₄. Normal: 1600W, Cool: 600W

Analyte	7500cs - ORS ICP-MS		7500s Non-cell ICP-MS	
	Mode	BEC ppt	Mode	BEC ppt
Ti (47)	Helium	49	Normal	1900
Cu (63)	Helium	0.3	Cool	2
Zn (68)	Helium	8	Normal	1900

Instrumentation

The instrument used in this application was an Agilent 7500cs ICP-MS fitted with a PFA Inert Kit. The PFA Inert Kit (Agilent part number G3139A #301) consists of a PFA-100 high efficiency, self-aspirating micro-flow nebulizer, 35 mm PFA end cap, 35 mm PFA spray chamber and an O-ring free demountable quartz torch, fitted with a 2.0-mm diameter platinum injector.

The 7500cs features Agilent's unique digital drive, crystal controlled, all solid-state 27.12MHz ICP RF generator, offering excellent stability for organic sample types and maintenance-free operation. The ShieldTorch (STS), which is fitted as standard and remains in place at all times, reduces the mean ion energy to approx 1eV, with a spread of ± 1eV. This allows the ORS to work much more efficiently in collision mode. The small energy spread of the ions entering the cell allows more efficient removal of lower energy polyatomic species by energy discrimination (ED). Since all polyatomic species are larger than monatomic analyte ions, they lose more energy in the cell than analyte ions due to collisions. Thus interference removal in collision mode is based on ionic radius and so is not matrix-specific or species-specific.

Another important feature of the 7500cs design is the ion optic. The 7500cs features a new dual extraction lens design that can be operated at positive voltage. Older extraction lens designs operate at a relatively high negative voltage, that extracts easily ionized elements (EIEs) from the secondary discharge inside the skimmer cone orifice, giving rise to elevated BECs. Operating in cool plasma mode, this has not been an issue since the

secondary discharge does not occur, and EIE BECs are low-ppt level. The extraction lens used in the 7500cs allows cool plasma-type EIE BECs to be achieved even at 1600W RF power, so all applications can be performed at 1600W.

Behind the extraction lens assembly is a new Omega lens that bends the ion beam off-axis into a new high transmission ORS cell, mounted on the same axis as the analyzer quadrupole. Both the extraction lens and Omega lens are mounted on the skimmer base and can be removed for maintenance without the need to open the vacuum system.

Data was acquired using a sequence of no-gas, H₂ mode and He mode within each sample. In both gas modes, the same cell gas flow rate of 5 mL/min was used in all cases. RF Power was set at 1600W for all measurements. Sample to sample run time was approximately 3 minutes. Data for each analysis mode is automatically combined into a single report using the Multi-tune software feature.

For more information on the 7500cs systems design, see reference 1.

Sample Preparation

Sample preparation consisted of simply diluting the concentrated H₂SO₄ 98% (w/w) with ultrapure deionized water resulting in a 9.8% (w/w) solution.

Method of Quantification

Analyses were performed using the method of standard additions (MSA) on an ultrapure-grade H₂SO₄ sample. The added spike concentrations in the final solution were 0, 2, 4, and 10 ppt. No internal standards were added to avoid the risk of contamination. The concentration of the analytes in the ultrapure-grade H₂SO₄ was calculated from the standard addition calibration curve. If a batch of H₂SO₄ samples is to be analyzed, the MSA curve can be converted into an external calibration curve so as to eliminate the need to create an MSA curve by spiking each sample to be analyzed. Once an external calibration curve is established from the MSA curve in this way, then all other sample concentrations can be determined with it. Concentrations obtained were corrected to account for the 10× dilution factor. Samples were spiked at a level of 5 ppt (ng/L) to assess the accuracy of the measurement.

Results

Figure 1 illustrates a representative calibration curve for Zn in 9.8% H₂SO₄ (w/w). Table 3 summarizes the H₂SO₄ detection limits (DL) obtained during this study. DLs were calculated using three times the standard deviation (n=3) of the raw counts in the H₂SO₄ divided by the slope of the MSA curve. Using the slope of the MSA curve, rather than counts obtained from a standard, takes into account any matrix suppression. The reported DLs are generally excellent and are dependent upon the trace metal content in the blank. This provides opportunity for even further improvement upon the reported values.

Spike recovery data at the 5 ppt (ng/L) level in 9.8% sulfuric acid is also given in Table 3. The spike recoveries are very impressive, particularly for difficult elements such as Ti (spike recovery at 50 ppt), Cr and Zn. This may be attributed to the reduction in sulfur based polyatomic interferences resulting from the effectiveness of the ORS.

The higher DL and BEC results for Ti may be due to contamination in the H₂SO₄. Other elements that suffer from sulfur-based interferences, such as Cr, Ni, Zn, and Cu show excellent BEC and DL values, which indicates successful removal of the interferences by the ORS.

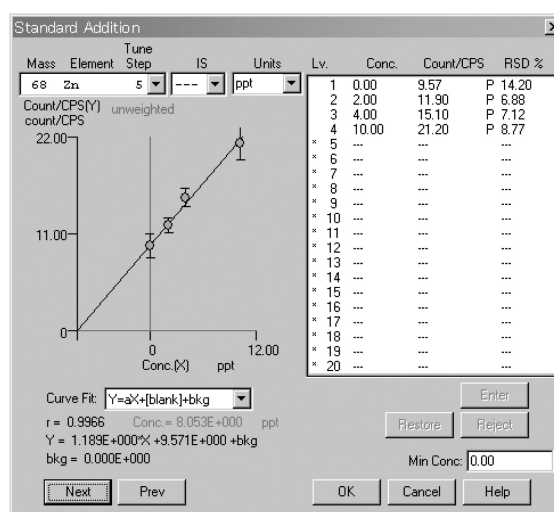


Figure 1. Zinc calibration curve in 9.8% H₂SO₄.

Table 3. DLs (3 sigma) and BECs and spike recoveries at 5 ppt level for all SEMI elements in 9.8% H₂SO₄

Element (mass)	Plasma power	H ₂ Gas flow (mL/min)	He gas flow (mL/min)	DL 3 sigma, n = 10 (ppt)	BEC (ppt)	SEMI* Tier C Spec - Max level	Spike recovery (%) 5 ppt spike
B (11)	Normal	—	—	1.6	12	100	107
Na (23)	Normal	5.0	—	0.7	6.2	100	140
Mg (24)	Normal	—	—	0.1	0.40	100	89
Al (27)	Normal	5.0	—	0.6	1.4	100	113
K (39)	Normal	5.0	—	2.8	14	100	95
Ca (40)	Normal	5.0	—	3.1	21	100	106
Ti (47)	Normal	—	5.0	27**	49**	100	87***
Cr (52)	Normal	—	5.0	1.0	7.4	100	98
Mn (55)	Normal	5.0	—	1.6	3.4	100	87
Fe (56)	Normal	5.0	—	1.6	8.9	100	92
Ni (60)	Normal	—	5.0	0.3	0.25	100	99
Cu (63)	Normal	—	5.0	0.2	0.28	100	87
Zn (68)	Normal	—	5.0	2.2	8.1	100	83
As (75)	Normal	—	5.0	0.6	0.29	100	93
Sn (118)	Normal	—	—	0.4	0.91	100	104
Sb (121)	Normal	5.0	—	0.8	2.0	100	100
Ba (138)	Normal	—	—	0.08	0.15	100	100
Pb (208)	Normal	—	—	0.5	2.2	100	95

*Maximum acceptable levels in undiluted H₂SO₄. **Suggests slight contamination of H₂SO₄. ***Ti recovery at 50 ppt level.

Data highlighting the differences for EIE measurement acquired at 1600W (normal plasma) and 600W (cool plasma) are summarized in Table 4. The new ion lens system on the 7500cs eliminates the extraction of these EIE from the interface region when high RF power is used. Though BEC and DL values obtained at high power for EIE are slightly higher than with cool plasma, this data clearly demonstrates the ultratrace measurement of Na, Mg, Al, and K at high plasma power (1600W).

A short-term stability study was performed by adding a 50 ppt standard into the 9.8% H₂SO₄ and analyzing the spiked sample over a 2-hour period. Instrument stability over this period was excellent with %RSD values typically 3%–4 %. A stability plot of representative elements is shown in Figure 2.

Table 4. Comparison of DLs (3 sigma) and BECs for EIEs in 9.8% H₂SO₄ acquired using cool and normal plasma power. H₂ was added at a flow rate of 5.0 mL/min

Element (mass)	DL (ppt)		BEC (ppt)		% Recovery - Cool	% Recovery - Normal
	Cool	Normal + H ₂	Cool	Normal + H ₂		
Na (23)	0.6	0.7	3.9	6.2	108	140
Mg (24)	0.07	0.1	0.1	0.40*	85	89
Al (27)	0.1	0.6	1.0	1.4	101	113
K (39)	0.9	2.8	8.3	14*	105	95
Ca (40)	1.1	3.1	5.8	21	85	106
Fe (56)	1.3	1.6	2.8	8.9	106	92

* No reaction gas was used.

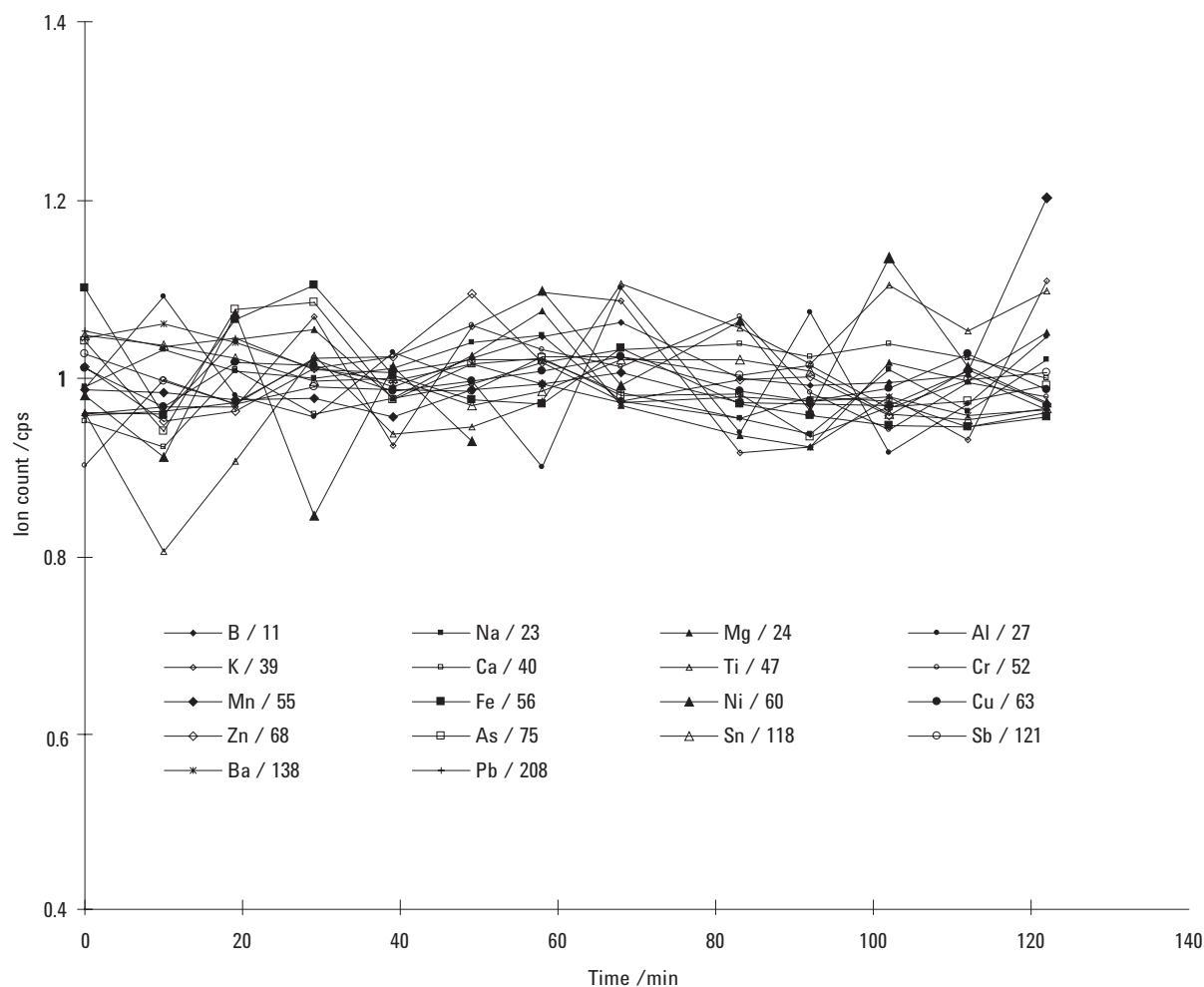


Figure 2. Analysis of 50 ppt multi-element standard spiked into 9.8% H₂SO₄ measured repeatedly over a 2-hour period. Analysis time per sample including 60 s of sample uptake was 185 s (0.33 s integration time, except Ti - 1 s, three repetitive measurements).

Conclusions

A newly developed high sensitivity reaction cell ICP-MS was used to analyze 98% (w/w) H_2SO_4 following a 10-fold dilution for elements specified in SEMI C44-0301: Specifications and Guidelines for Sulfuric Acid. The Agilent 7500cs features a new-design ion lens system for high ion transmission and an ORS cell for interference removal. By pressurizing the cell with simple gases, hydrogen and helium, plasma and sulfur-based polyatomics are removed, allowing the direct, ppt-level measurement of all SEMI elements, including Ti, Cu, and Zn in H_2SO_4 . All measurements were made on mass, avoiding the uncertainty associated with measuring analyte cluster ions formed in the cell.

The Micro Flow nebulizer combined with the highly efficient new Omega lens system enables the direct aspiration of 9.8% (w/w) H_2SO_4 while maintaining excellent sensitivity, good signal stability and reducing interface wear. The new extraction lens design also reduces EIE BECs to cool plasma levels even at 1600W forward power. All applications can be performed at a single, high power setting with the added advantage of excellent cool plasma performance still being available for those users who have existing and proven methodology based on the technique.

The DL, BEC, spike recovery and stability data presented in the application note highlight the suitability and accuracy of the Agilent 7500cs to determine ppt level impurities in H_2SO_4 for all of the important SEMI specified elements. All analytes were measured, in a single analytical run with automatic switching of cell and plasma parameters. A typical total analysis time for this application is 4 minutes. All data is automatically combined into a single report.

Samples were analyzed using the MSA. Only the first sample is spiked with the calibration standards and a MSA regression is generated which is then converted to an external calibration curve. This method eliminates the need to spike all subsequent samples, so aiding sample throughput.

References

1. (2003) *Agilent ICP-MS Journal Issue 15*, Agilent Technologies publication 5988-8983EN
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